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The oxidative decarboxylation of aminopolycarboxylic acids with cerium (IV) in sulfuric acid

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THE OXIDATIVE DECARBOXYLATION OF AMINOPOLYCARBOXYLIC ACIDS WITH CERIUM(IV) IN SULFURIC ACID

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II. A Comparative Kinetic Study of the Oxidation of NTA, EDTA, CDTA and DTPA with Cerium (IV) in Sulfuric Acid Media

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Summary. The rates of oxidation of four chelating agents, NTA, EDTA CDTA, and DTPA with Ce(IV), in sulfuric acid media, were determined spectrophotometrically by a stopped-flow technique. The reductive ability is in the order CDTA>EDTA>DTPA>NTA. The influence of varying the acidity of the medium was studied, and in each case a maximum in the rate constant vs. $[H^+]$ plot was observed. A possible interpretation of the reactivities and the influence of acidity is advanced.

Oxydative Decarboxylierung von Polyaminocarbonsäuren. II. Vergleichende kinetische Untersuchung der Oxydation von NTA, ÄDTA, CDTA und DTPA mit Ce(IV) in saurer Lösung. Die Oxydationsgeschwindigkeiten von 4 Chelaten (NTA, ÄDTA, CDTA und DTPA) mit Ce(IV) in saurer Lösung wurden spektrophotometrisch mit Hilfe der „stopped-flow"-Technik bestimmt. Die Reduzierfähigkeit nimmt in der Reihenfolge CDTA > ÄDTA > DTPA > NTA ab. Der Einfluß verschiedener Säuregehalte in der Lösung wurde untersucht, und in jedem Fall wurde ein Maximum in der graphischen Darstellung der Geschwindigkeitskonstante gegen $[H^+]$ beobachtet. Eine mögliche Erklärung des Reaktionsvermögens und des Säureeinflusses wird gegeben.

Introduction

In part I of this series we reported [3] on the stoichiometry and the kinetics of the reaction of ethylenedinitrilotetraacetic acid (EDTA), in acid media, with Ce(IV). As a continuation of the previous work we wish to relay our results on the comparative ease of oxidation, with Ce(IV) in sulfuric acid media, of several polyaminocarboxylic acids usually used as chelating agents, in the decontamination of living organisms, and recently involved in antipollution detergents.

Experimental

Reagents. Ceric ammonium tetrasulfate $(NH_4)_4\ Ce(SO_4)_4$, ethylenedinitrilotetraacetic acid, EDTA (Titriplex III), nitrilotriacetic acid, NTA (Titriplex I), 1,2-cyclohexyldiaminetetraacetic acid, CDTA (Titriplex IV), and diethylenetriaminepentaacetic acid, DTPA (Titriplex V) were all Merck reagent grade chemicals of the highest purity and were used without further purification.

Procedure. The rates of reaction between Ce(IV) and the 4 chelating agents were studied spectrophotometrically at 316 nm by following the consumption of Ce(IV), using a Durrum-Gibson stopped-flow apparatus. The initial concentrations in the reaction mixture were 1×10^{-4} M Ce(IV) and 1×10^{-2} M chelating agent for most of the studies. The acidity of the medium, H^+, was varied from a low of 0.04 M to a high of 5.0 M. Each rate measurement was repeated several times to insure reproducibility. The half-life of Ce(IV) was read directly from the oscilloscope screen displaying percentage transmission vs. time (Fig. 1). The first-order rate constants were calculated from the formula, $k_1 = 0.693/t_{\frac{1}{2}}$. The chelating agent was always in such an excess that its concentration

Figure 1

The oscilloscope trace of the change in percent transmission vs. time for the Ce(IV)-CDTA system, recorded at 316nm

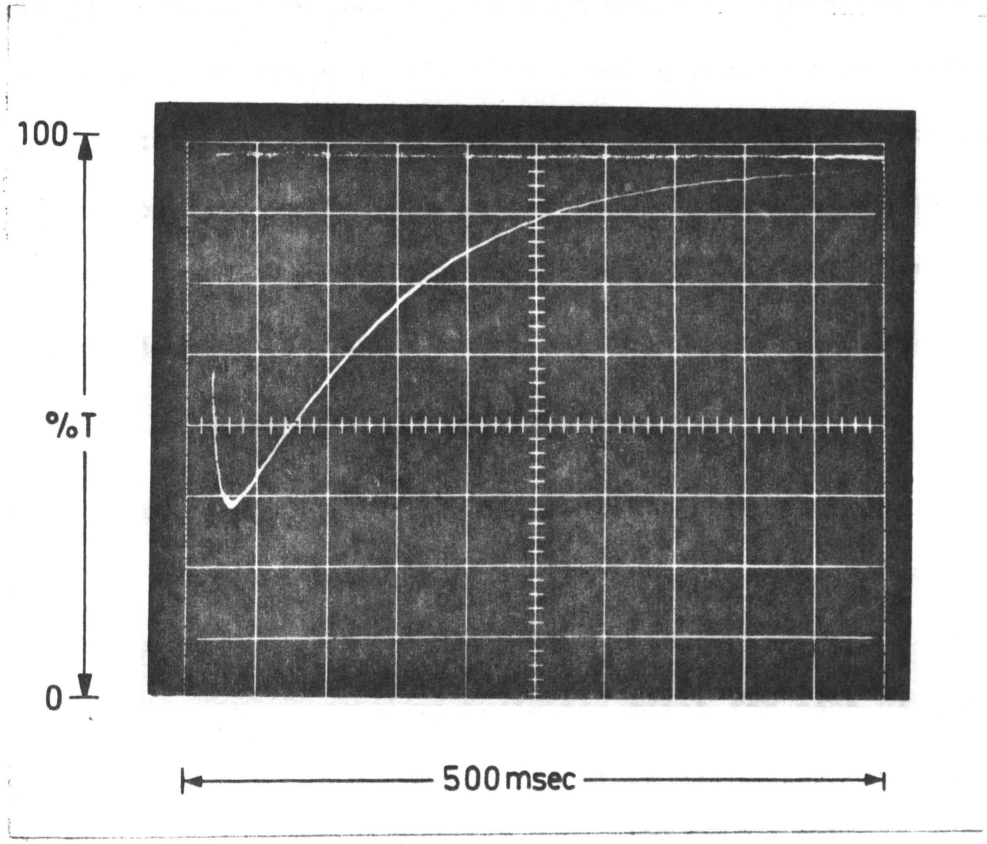

Fig. 1

did not vary by more than 1-2% when the Ce(IV) was already half consumed. The second-order rate constants, k_2, were calculated by dividing k_1 by[Titriplex]$_o$ in any particular run. Second-order rate constants were reproducible to better than $\pm$ 5%.

Results and Discussion

The rates of reduction of Ce(IV), in acid media by chelating agents which differ substantially in their complexing powers were studied spectrophotometrically. In the region of concentrations workable in UV spectrophotometry, variations in the initial concentrations of reactants at a fixed hydrogen ion concentration (Table 1) lead to a second-order kinetic equation

$$\frac{dCe(IV)}{dt} = k_2[Ce(IV)]\,[Titriplex]$$

With fixed initial concentrations of reactants, the changing of the acidity of the medium had a remarkable influence on the rates of reactions. The variation of k_2 with $[H^+]$ is shown in Fig. 2 for the 4 chelating agents. We observe an inflexion point for each of the chelating agents at a characteristic $[H^+]$: between 0.09 and 0.10 M for CDTA, about 0.8 M for NTA, about 1.5 M for DTPA, and between 1.0 and 1.5 M for EDTA. Similar behavior has been reported [1] in the oxidation of Fe(II) by Ce(IV), and recently in the oxidation of Sb(III) by Ce(IV) in perchloric acid medium [5].

The latter workers explained their results in terms of the various equilibria involving Ce(IV) in perchloric acid media. In view of the known increase in the oxidation potential of Ce(IV) with increasing acid concentration [6] we believe that the decrease in rate with increasing $[H^+]$, shown in Fig. 2, is probably mainly due to protonation of the polyaminocarboxylic acids which would render them inactivated towards

Table 1. Second-Order Rate Constants for the Reduction of Ce(IV) by Different Chelating Agents at a Fixed $[H^+]$ = 2.5 M at 25 ± 0.05°C.

Chel. Agent	Run No.	$[Ce(IV)]_o$ M x 10^4	$[Titriplex]_o$ M x 10^3	$10^3 k_2$, M^{-1} sec^{-1}
NTA	261	1.00	2.50	2.20
	262	1.25	2.50	1.98
	277	1.00	5.00	1.98
	279	2.00	5.00	1.98
	240	0.75	10.00	1.93
	292	0.75	15.00	2.10
	295	2.00	15.00	1.89
EDTA	281	1.00	5.00	28.80
	282	1.25	5.00	28.80
	283	2.00	5.00	31.50
	248	2.00	10.00	31.50
	299	1.25	15.00	30.80
CDTA	271	2.00	2.50	44.00
	285	1.00	5.00	46.20
	251	1.00	10.00	45.60
	253	2.00	10.00	46.20
	302	1.00	15.00	44.00
DTPA*	272	0.75	2.50	33.80
	274	1.25	2.50	33.00
	286	1.00	5.00	33.80
	288	2.00	5.00	34.60
	257	1.25	10.00	33.00
	258	2.00	10.00	33.00
	307	1.25	15.00	35.60

*The higher k_2 for DTPA compared to EDTA might seem inconsistent with the statement in the Summary concerning the relative reactivities of the 2 chelating agents towards oxidation by Ce(IV). Those reported relative reactivities refer to the inflexion points in the k_2 vs. $[H^+]$ plot (Fig. 2). It is evident from that plot that, at $[H^+]$ to the right of the inflexion points, the order of reactivity changes for these 2 chelating agents.

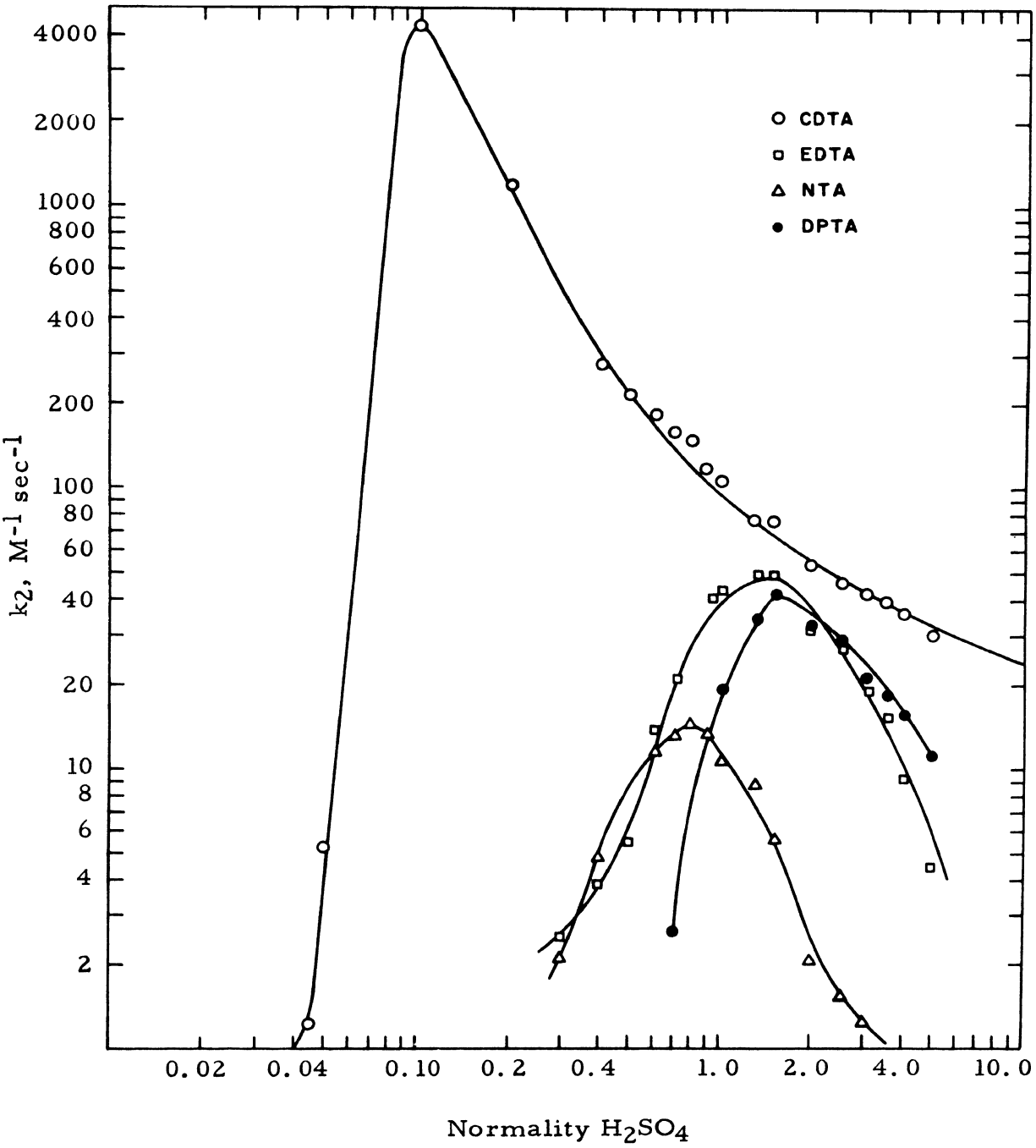

Fig. 2. Logarithmic relationship of the Ce(IV) - Titriplex second-order rate constants and the acidity of the medium.

complexation with Ce(IV) and towards oxidation. The lone pair of electrons on the nitrogen of the chelating agents is probably the source of the reductive ability of these agents. Protonation constants of 12.6, 25.1, and 52.5, and NTA, EDTA, and CDTA respectively, recently reported by Anderegg [2], suggest that these chelating agents are heavily protonated at, and beyond, the particular inflexion points, and thereby deactivated in relatively strong acid media.

The much higher reductive ability of CDTA as compared to the other chelating agents may be readily explained in terms of the favorable and fixed geometry of the nitrogen ligands in CDTA which allows for easy interaction with Ce(IV). The hindered rotation around C_1-C_2 in 1,2-cyclohexyldiaminetetraacetic acid in contrast to the freely rotating EDTA, apparently endows the CDTA molecule with the most favorable geometry for complexation. We are inclined to believe that such complexation, which may be a necessary step in the oxidative decarboxylation process involves the 2 nitrogens primarily and that CDTA provides the ideally needed stereoelectronic environment.

Attempts to measure rates of formation of a Ce(IV) complex with EDTA failed with the available instrumentation. Complex formation, detected spectrophotometrically with EDTA but not with CDTA, was too fast to measure by the ordinary stopped-flow technique. However, with DTPA where conformational adjustments are probably needed for complexation with Ce(IV), the rates of such complexation and of the decay of the complex to Ce(III) and DTPA oxidation products have been measured conveniently at room temperature. At $[H^+]$ = 0.6 M the half-life of complex formation between 10^{-4} M Ce(IV) and 10^{-2} M DTPA is 35 milliseconds; the half-life for complex decay is 76 seconds. The details of this study at different H^+ and different temperatures are reported elsewhere [4].

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A KINETIC STUDY OF THE COMPLEX FORMATION AND OXIDATION OF DIETHYLENETRIAMINEPENTAACETIC ACID (DTPA) WITH CERIUM(IV) IN SULFURIC ACID MEDIA

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Polyaminocarboxylic acids, commonly used as chelating agents, are known to form complexes with trivalent lanthanides, and such complexes have been studied extensively (1). On the other hand, very little is known about complexes with Ce(IV). In a limited acid range, an unstable Ce(IV)-EDTA complex has been reported (2,3). Hafez and Guillaumont referred briefly to the reduction of Ce(IV) by DTPA and the formation of a Ce(III)-DTPA complex (4).

This paper presents what we believe is the first rate study of complex formation between Ce(IV) and a polyaminocarboxylic acid, diethylenetriaminepentaacetic acid (DTPA). Like EDTA (2), DTPA reduces Ce(IV) in acid media. The kinetics of this reaction were studied by following the disappearance of Ce(IV) spectrophotometrically at 316 nm using a stopped-flow technique (5). The rate is first order in each reactant and exhibits a maximum in its dependence on $[H^+]$ at about 0.75 M H_2SO_4 (5). It was observed, however, in oscilloscope traces of % transmission vs. time, that for reactions conducted at $[H^+] \leq 1.5$ M there was a rapid decrease in optical density at 316 nm immediately after mixing followed by a slower decrease (Fig. 1, curve a).

This phenomenon, observed at various temperatures and for various concentrations of DTPA, but not detectable at $[H^+] \geq 1.5$ M, led us to suspect

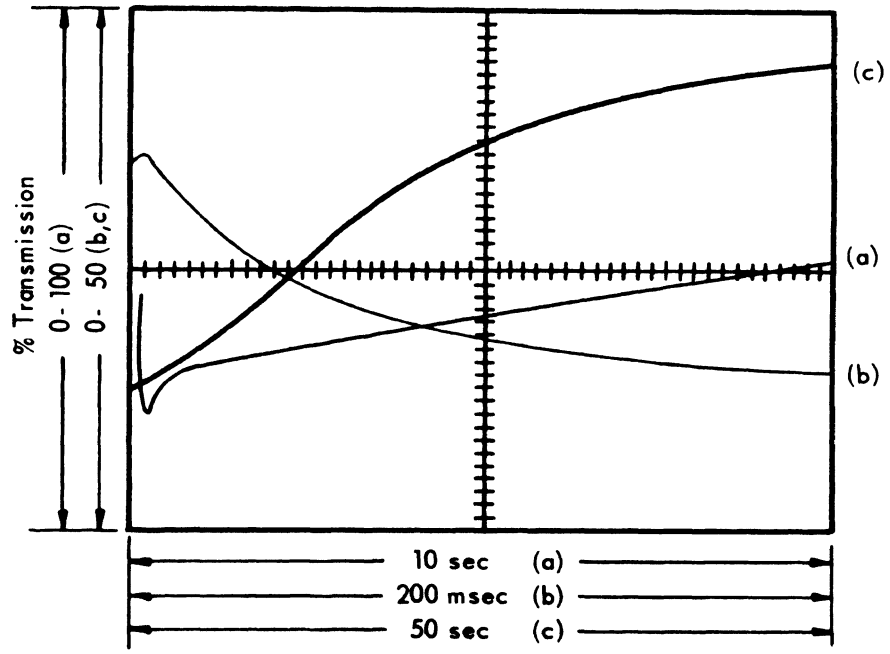

FIG. 1
Oscilloscope Traces of % Transmission vs Time for
(a) Ce(IV) reduction by DTPA at 316 nm
(b) Ce(IV)-DTPA complex formation at 264 nm
(c) Ce(IV)-DTPA complex decay at 264 nm.

the occurrence of a consecutive reaction with a relatively fast first step. We entertained the possibility of complex formation as the first step. Solutions of Ce(IV) in 0.025 M H_2SO_4 which ordinarily show a strong absorption at 316 nm ($\epsilon = 5.77 \times 10^3$) showed a different, strong but broad, absorption centered at 264 nm when mixed with DTPA (Fig. 2). There is practically no interference at this wavelength from Ce(IV), Ce(III), which has a very weak absorbance at 252 nm ($\epsilon = 500$), DTPA or its oxidation products. The species absorbing at 264 nm, presumably a complex between Ce(IV) and DTPA, was relatively stable at 0.025 M H_2SO_4 but decayed at measurable rates with increasing $[H^+]$. Such species was not detectable at $[H^+] \geq 1.5$ M.

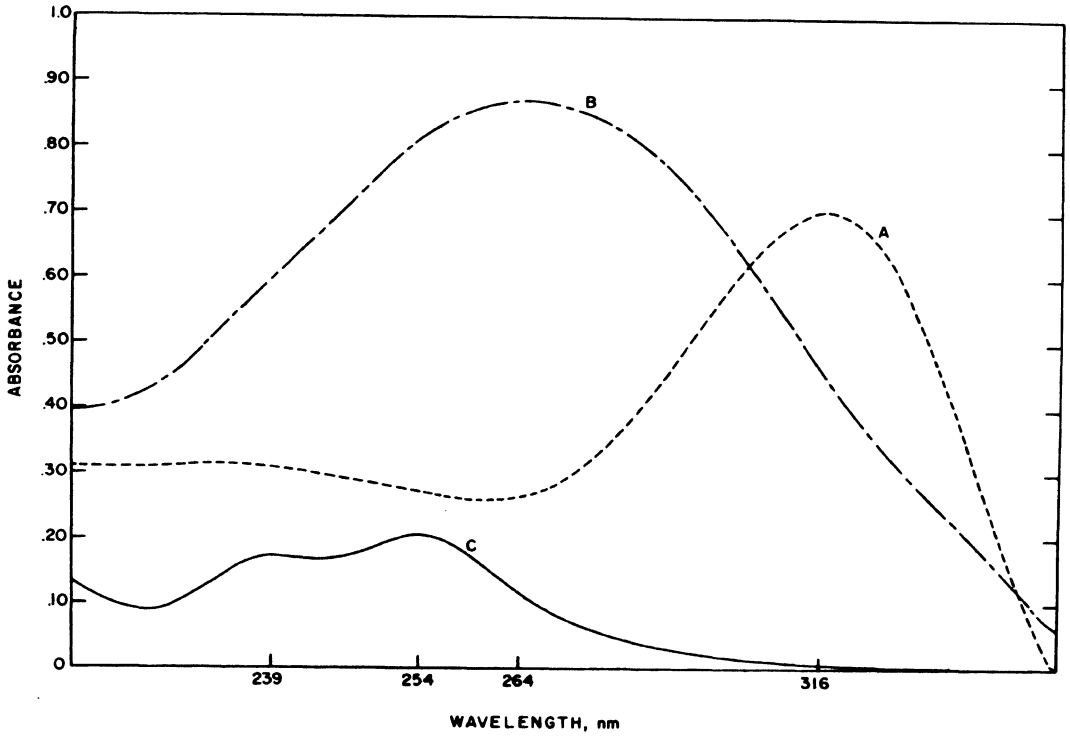

FIG. 2

UV Absorption Spectra for (a) Ce(IV) in aq. H_2SO_4
(b) Mixture of Ce(IV) and DTPA
(c) The same as (b), 20 min. later.

TABLE 1

Observed First-Order Rate Constants ($k_1 = 0.693/t_{\frac{1}{2}}$) for the Formation and Decay of the Ce(IV)-DTPA Complex at 264 nm at 25°C.

$[Ce(IV)]_o = 1 \times 10^{-4}$ M; $[DTPA]_o = 1 \times 10^{-2}$ M

$[H^+]$, M	Complex Formation		Complex Decay	
	$t_{\frac{1}{2}}$ msec	k_1, sec^{-1}	$t_{\frac{1}{2}}$ sec	$10^2 k_1$, sec^{-1}
0.4	10.0	69.3	slow	
0.6	35.0	19.8	76.4	0.91
0.7	65.0	10.7	38.0	1.83
0.8	95.0	7.30	13.5	5.12
0.9	140	4.96	10.0	6.93
1.0	170	4.07	6.2	11.2
1.3	180	3.86	3.0	23.1
≥1.3	no complex formation observed			

Inspection of the rate data in the Table reveals that the rates of

complex formation (Fig. 1, curve b) and complex decay to Ce(III) (Fig. 1, curve c) are affected in opposite directions with increasing $[H^+]$. The inhibiting effect of H^+ in complex formation is readily explained in terms of the H^+ released on complexation:

$$Ce(IV) + H_4DTPA \rightleftarrows Ce(IV)\text{-}DTPA + 4\ H^+.$$

High acidity would inhibit complex formation through protonation of the amino nitrogens and, in H_2SO_4 media, also possibly through coordination of the $SO_4^=$ to form relatively stable $Ce(IV)\text{-}SO_4^=$ species. The reason for catalysis by H^+ of the decay of the complex to Ce(III) is less evident but may be taken as indicative of the participation of protonated complex species as was suggested in the study of the decomposition of the EDTA-Ce(IV) complex (3). The stability of the complex at lower $[H^+]$ may be due to the formation of hydroxy species which tend to stabilize the tetravalent state.

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THE OXIDATIVE DECARBOXYLATION OF POLYAMINOCARBOXYLIC ACIDS-III. A STUDY OF THE REACTION OF DIETHYLENETRIAMINEPENTAACETIC ACID (DTPA) WITH CERIUM(IV) IN SULFURIC ACID MEDIA

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Summary - The oxidation of diethylenetriaminepentaacetic acid by Ce(IV) in sulfuric acid was investigated spectrophotometrically by the stopped-flow technique. The rate of reaction is influenced by variations in acidity of the media, but can be expressed by a simplified rate law:

$$-\frac{d[Ce(IV)]}{dt} = k'[Ce(IV)][DTPA]$$

in which k' is calculated from the variations in the observed rate with the acidity of the media. Below 0.75M H_2SO_4 the reaction follows a step-wise mechanism as evidenced by the formation of a 1:1 Ce(IV)-DTPA complex whose rate of formation and decay are measurable. At higher acid strengths, the formation of an intermediate is not evident. The rate of consumption of Ce(IV) by DTPA is maximum at ≈0.75M H_2SO_4. The data are interpreted in terms of the relative concentrations of the various species in the H_2SO_4 media. In the initial reaction, one equivalent of Ce(IV) is consumed per equivalent of DTPA; the overall stoichiometry varies with time.

It has been known for some time that Ce(IV) is a very strong and versatile oxidizing agent.[1] Many studies have been reported on its

use in the oxidation of metal ions, mineral and organic acids, and other organic compounds in a variety of media.[2] Interest in Ce(IV) oxidations of aminocarboxylic acids is more recent,[3,4,5] due perhaps, in this case, to their primary function as reducing rather than chelating agents. We have undertaken a comprehensive study of the oxidation of polyaminocarboxylic acids with Ce(IV) in acid media. The rates and mechanisms of the oxidation of EDTA and a comparative rate study of CDTA, DTPA, EDTA, and NTA oxidations have been conducted in these laboratories.[6,7] Spectrophotometric evidence that complex formation occurs at a measurable rate in the oxidation of DTPA[8] prompted us to focus further attention on that reaction. This paper deals with a stoichiometric study of both complex formation and the reduction of Ce(IV) by DTPA, and with a rate study of the two processes in H_2SO_4 media.

EXPERIMENTAL

Reagents

Ceric ammonium tetrasulfate and diethylenetriaminepentaacetic acid were pro analysi Merck reagents; sulfuric acid was Fisher reagent grade. Acid media were prepared by dilution from a standardized H_2SO_4 solution; a standardized solution of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ in 0.0986N H_2SO_4 was diluted to desired concentrations of Ce(IV). Aqueous diethylenetriaminepentaacetic acid solutions of known concentrations were prepared by direct weighing. Solutions of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ were also prepared by direct weighing of the salt, and a standard procedure[9] was followed in preparing the o-phenanthroline indicator. All chemicals were of the highest quality and used without further purification.

Apparatus and procedure

Stoichiometry of the Ce(IV)-DTPA reaction. The number of moles of Ce(IV) consumed per mole of DTPA was determined at several acidities and with time both by spectrophotometric and titrimetric studies. In spectral studies, the consumption of Ce(IV) with time was followed at 316nm on a Beckman DK-2A spectrophotometer equipped with a time-drive attachment. Known volumes of 2.0×10^{-4} M Ce(IV) and 2.0×10^{-4} M DTPA were mixed rapidly and the decrease in the absorbance of the solution was recorded with time. Cerium(IV) solutions in 0.1M, 0.6M, 0.7M, 1.3M, 1.5M and 2.0M H_2SO_4 were used to study the dependence of the stoichiometry on the acidity of the media.

To follow the stoichiometry titrimetrically, known volumes of standardized Ce(IV) were mixed thoroughly with a fixed volume (5 ml) of DTPA at room temperature for specific periods of time. The reactions were quenched with excess of measured volumes of 0.100M standard Mohr's salt, and the number of equivalents of DTPA in the initial reaction was determined by back-titration of the Fe(II) with Ce(IV) using o-phenanthroline as indicator.

Stoichiometry of complex formation. Investigations of the stoichiometry of the Ce(IV)-DTPA complex were carried out on a Beckman DK-2A spectrophotometer, a Cary -14 spectrophotometer, and a Sargent automatic recording titrimeter. Standard procedures[10] were followed for the continuous variations and molar-ratio determinations. For the method of continuous variations, the total concentration of the mixed reactants was 2.0×10^{-4} M. For molar ratio studies, the concentration of Ce(IV) was fixed at 2.0×10^{-4} M in 0.1 M H_2SO_4 and the concentration of aqueous DTPA was varied from 1.0×10^{-4} M to 6×10^{-4} M. The UV

spectra of the reactants in 1-cm path silica cells were recorded over the range of 400nm to 230nm at 30°C. The absorbance of the complex formed in each case was read at 264nm.[8] For all spectra, the reference cell contained sulfuric acid of the same concentration as that used in preparing the Ce(IV) solutions.

Following the procedure outlined by Flaschka,[11] potentiometric titrations were also carried out to determine the stoichiometry. Solutions of 2.0×10^{-3} M Ce(IV) in 0.1 M H_2SO_4 were titrated with 2.0×10^{-2} M DTPA, or alternately, an acidified solution of 2.0×10^{-3} M DTPA was titrated with 2.0×10^{-2} M Ce(IV) in 0.1 M H_2SO_4.

Kinetics of the Ce(IV)-DTPA reaction. The rates of the reaction between Ce(IV) and DTPA were followed spectrophotometrically with a Durrum-Gibson stopped-flow spectrophotometer with a Tektronix oscilloscope attachment. A polaroid camera was used to make permanent records of the oscilloscope traces of percent transmission vs. time. The consumption of Ce(IV) was followed at 316nm where the Ce(IV) species obeys Beer's Law and where there is no appreciable interference from DTPA, the media, or the reaction products. A thermostated circulating water bath was used to maintain the solutions at the desired temperature $\pm$ 0.05°C. By keeping [DTPA] in large excess, first-order rate constants were calculated for the reaction from the half-life of Ce(IV) recorded by the decrease in optical density vs. time. Second-order rate constants were obtained by dividing k_1 by [DTPA]. Because the rate calculated in this manner showed a varying dependence on the acidity, true rate constants were calculated by multiplying the observed rate by a function of the acid concentration.

Kinetic order of complex formation. The kinetics of complex formation was determined by measuring the absorbance at 264nm[8] as a function of variations in the initial concentrations of the reactants and of the acidity.

RESULTS AND DISCUSSION

Stoichiometry of the Ce(IV)-DTPA reaction, spectral studies

In our earlier work with EDTA[6] we observed that four moles of Ce(IV) were immediately consumed per mole of EDTA. It was expected then, that in a similar manner, DTPA would immediately reduce five equivalents of Ce(IV). Solutions of 5:1 Ce(IV)-DTPA in 0.7 M H_2SO_4 were scanned in the UV region from 340nm to 200nm immediately after mixing. In each case, measurable absorbance at 316nm indicated that some Ce(IV) remained unreduced and that the stoichiometry deviated from that extrapolated from the EDTA-Ce(IV) reactions. The appearance of absorbance peaks at 254nm and 239nm in the scans of the reaction mixture indicated that some Ce(III) was produced.[4] Repeated scans of the same solutions revealed a steady decrease in the absorbance of Ce(IV) accompanied by increased product absorbance. Spectra of equimolar quantities of both reactants showed absorbance only at the wavelengths attributed to Ce(III).

Effect of time. It was obvious from repeated scans of solutions of reaction mixtures containing excess Ce(IV) that the gradual decrease in the absorbance at 316nm was due to progressive reduction of Ce(IV). This was not surprising since we had observed the same phenomenon in the Ce(IV)-EDTA reaction,[6] and Rao[3] reported a large consumption of Ce(IV) by DTPA after several hours which confirmed our earlier obser-

vations.[12] Rao also reported that at least one product, glycine is not further oxidized by Ce(IV), but that other intermediate products are further oxidized to formic acid and CO_2. Jones and Lambert[13] reported that the oxidation of polyaminocarboxylic acids with $[Fe(CN)_6]^{3-}$ initially produces glyoxals and amines that are oxidized to glycine, formic acid and formaldehyde. We have previously observed both a positive test for formaldehyde in reaction solutions and that the reaction of excess 0.1 M ceric ammonium nitrate in 6 N H_2SO_4 with 0.1 M DTPA produced about 4 moles of CO_2.[12] Preliminary work with electrophoresis and paper chromatography indicates that symmetrical and unsymmetrical ethylenediaminediacetic acid, glycine, ethylenediamine, and 2-oxo-1-piperazineacetic acid are among the products of the oxidation of DTPA by Ce(IV).

When additional Ce(IV) was injected into solutions in which the first quantity of Ce(IV) had already been consumed (O.D. at 316nm = 0), the absorbance at 316nm reappeared, but decayed slowly as the absorbance at 254nm and 239nm simultaneously increased. By adjusting the time-drive attachment to record the reduction of Ce(IV) at 316nm, solutions with a known excess of Ce(IV) were time-scanned at that wavelength. In 0.6 M H_2SO_4, five equivalents of Ce(IV) were consumed in 5.25 minutes. When the initial concentration of Ce(IV) was ten times greater than that of DTPA, 75% of the Ce(IV) was consumed after one hour. Twenty-four hours later, no Ce(IV) remained in solution. After forty hours, no change in the absorbance peaks of the reaction mixture could be detected.

At higher acidities, the consumption of Ce(IV) was slower. For several trials, the complete reduction of a 5:1 excess in 1.3 M H_2SO_4

was observed after 41 minutes; in 2.0 M acid the same reduction required an average of 80 minutes. The slower consumption of Ce(IV) as the acidity was increased is in line with the earlier results[8] which showed that the rate of reduction of Ce(IV) was decreased beyond 0.75 M H_2SO_4. The extent of reaction immediately after mixing was calculated from a comparison with the absorbance of a Ce(IV) blank. From two experiments it was determined that about 20% of the Ce(IV) had been immediately consumed. This amount of Ce(IV) was equal, within 1 x 10^{-5} moles (5%), to the amount of DTPA in the reaction mixture.

Effect of acidity. Varying the acidity of the Ce(IV) solutions did not alter the initial stoichiometry of the reaction between Ce(IV) and DTPA. However, spectra of equal volumes of reactants in 0.1 M H_2SO_4 did not initially indicate the reduction of Ce(IV); rather, a strong absorbance appeared almost instantaneously at 264nm, characteristic of the relatively stable complex expected at low acidities.[8] After several hours, the only absorbance in those solutions was at 254nm and 239nm, characteristic of Ce(III). Spectra of equimolar mixtures in 0.65 M, 0.75 M, and 1.0 M H_2SO_4 showed no absorbance at 316nm presumably due to rapid reduction of Ce(IV). However, that absorbance reappeared when more Ce(IV) was introduced; the peak decayed with time.

Titrimetric studies. In order to further study the stoichiometry determined spectrophotometrically, known aliquots of 0.1 M DTPA were mixed with known volumes of 0.0933 M Ce(IV) in 1.7 M H_2SO_4 and immediately quenched by injecting excess Fe(II) into the reaction solutions. Back titration with Ce(IV) using o-phenanthroline as indicator showed

that, at room temperature, only one mole of Ce(IV) was consumed per mole of DTPA (Table I).

Table I shows results of reactions that were quenched in the same manner after specific periods of time. From the graphical representation of these data (Fig. 1) it can be seen that the quantity of Ce(IV) consumed in the reaction with DTPA increases with time, but increases slowly after about five minutes.

In view of the many oxidizable centers in the DTPA molecule, (I), the variable stoichiometry is not unusual. It is surprising, however, that while EDTA, (II), consumes 4 equivalents of Ce(IV), almost instantaneously, under conditions identical to those employed for the Ce(IV)-DTPA study, this latter system displays only a 1:1 reaction ratio (Table I) at the initial stages of interaction. It is possible, however, that the initial interaction between Ce(IV) and the chelating agent is much more sluggish in the DTPA case than in the EDTA system since the latter readily provides the 6 centers needed for hexadentate coordination. In the DTPA case, on the other hand, the molecule will have to undergo certain conformational adjustments before it can effectively provide the tetravalent cerium ion with the needed coordination. In support of this explanation in terms of conformational readiness of the chelating agent is the fact that CDTA (trans, 1,2 diaminocyclohexanetetraacetic acid, (III), which is endowed with the rigid, but most favorable geometry for complexation, undergoes oxidation with Ce(IV) at a rate which is about 100 times faster than EDTA or DTPA.

TABLE I.-EXTENT OF CONSUMPTION OF Ce(IV) BY DTPA IN 1.25M H_2SO_4 AS A FUNCTION OF TIME AT 25°C

Run No.	Concentration, M± [Ce(IV)]	Concentration, M± [DTPA]	Time, min.	Ce(IV) : DTPA
1-7	0.062*	0.033*	0	0.966*
11	0.076	0.020	2	3.486
12	0.076	0.020	2	3.486
13	0.082	0.014	5	5.102
14	0.082	0.014	5	5.122
15	0.082	0.014	10	5.254
16	0.082	0.014	10	5.216
17	0.082	0.014	10	5.274
18	0.082	0.014	30	5.682

± Concentration after mixing Ce(IV) and DTPA solutions

* Average of seven values

Figure 1

Consumption of Ce(IV) by DTPA with time

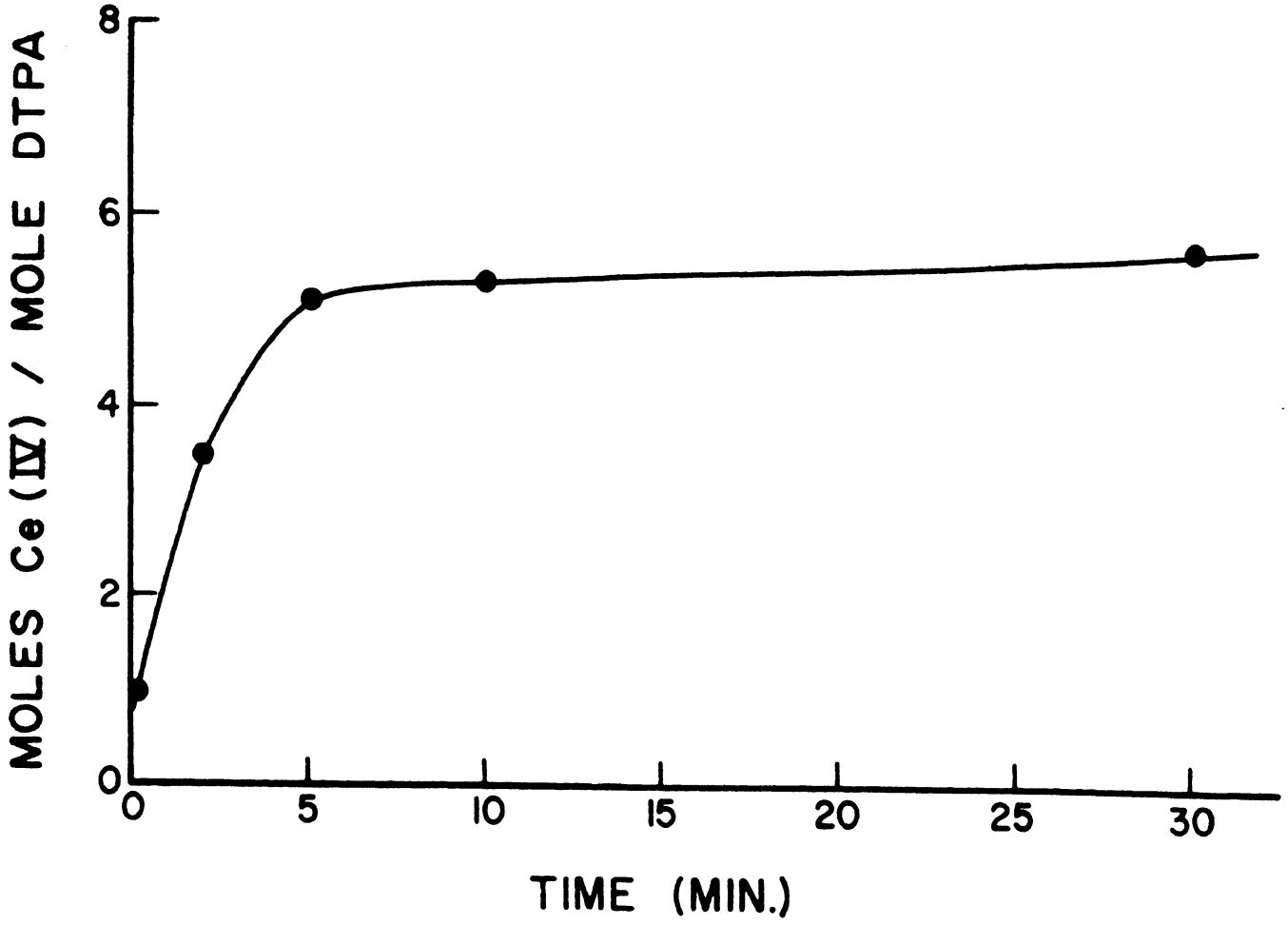
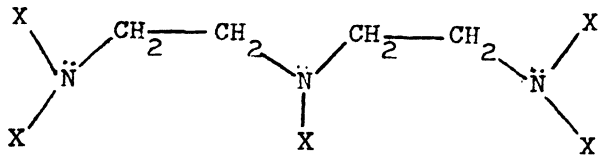
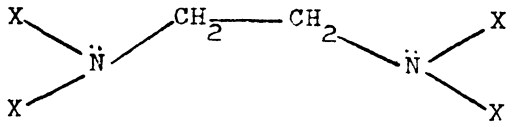


Fig. 1

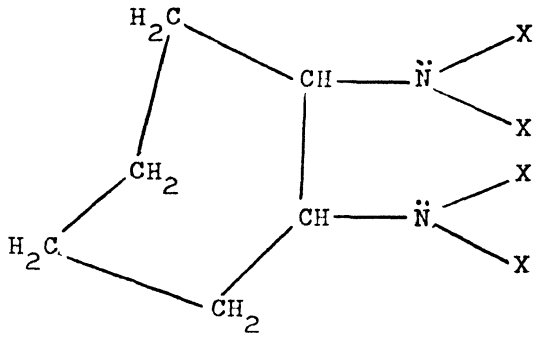
I



II



III



X = $-CH_2-CO_2H$

Stoichiometry of complex formation, spectral studies

The sharp initial decrease in the absorbance of Ce(IV) at 316nm when mixed with DTPA (Fig. 2) led us to suspect the rapid formation of a Ce(IV)-DTPA complex, and spectral studies showed that there was in fact a new strong absorbance, presumably of a complex, at 264nm.[8] Measurements were made to determine the metal : ligand ratio in the complex using both the continuous variations and molar ratio methods. Following standard procedures,[10] Ce(IV)/DTPA solutions in 0.05 M H_2SO_4 were mixed and the absorbances recorded. The graphs depicted in Figure 3 indicate a 1:1 complex between Ce(IV) and DTPA.

Potentiometric Studies. Flaschka[11] has shown that the stoichiometry of Fe(III)-EDTA complexes could be determined by continuously

Figure 2

Oscilloscope trace of the decrease in absorbance of Ce(IV) at 316nm when mixed with DTPA

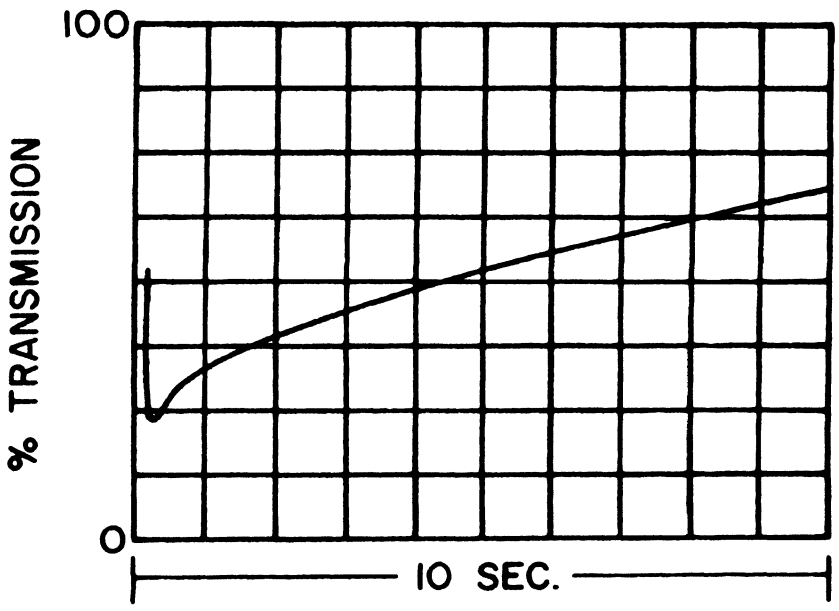


Fig. 2

Figure 3a

Continuous variations determination of the stoichiometry of the Ce(IV)-DTPA complex

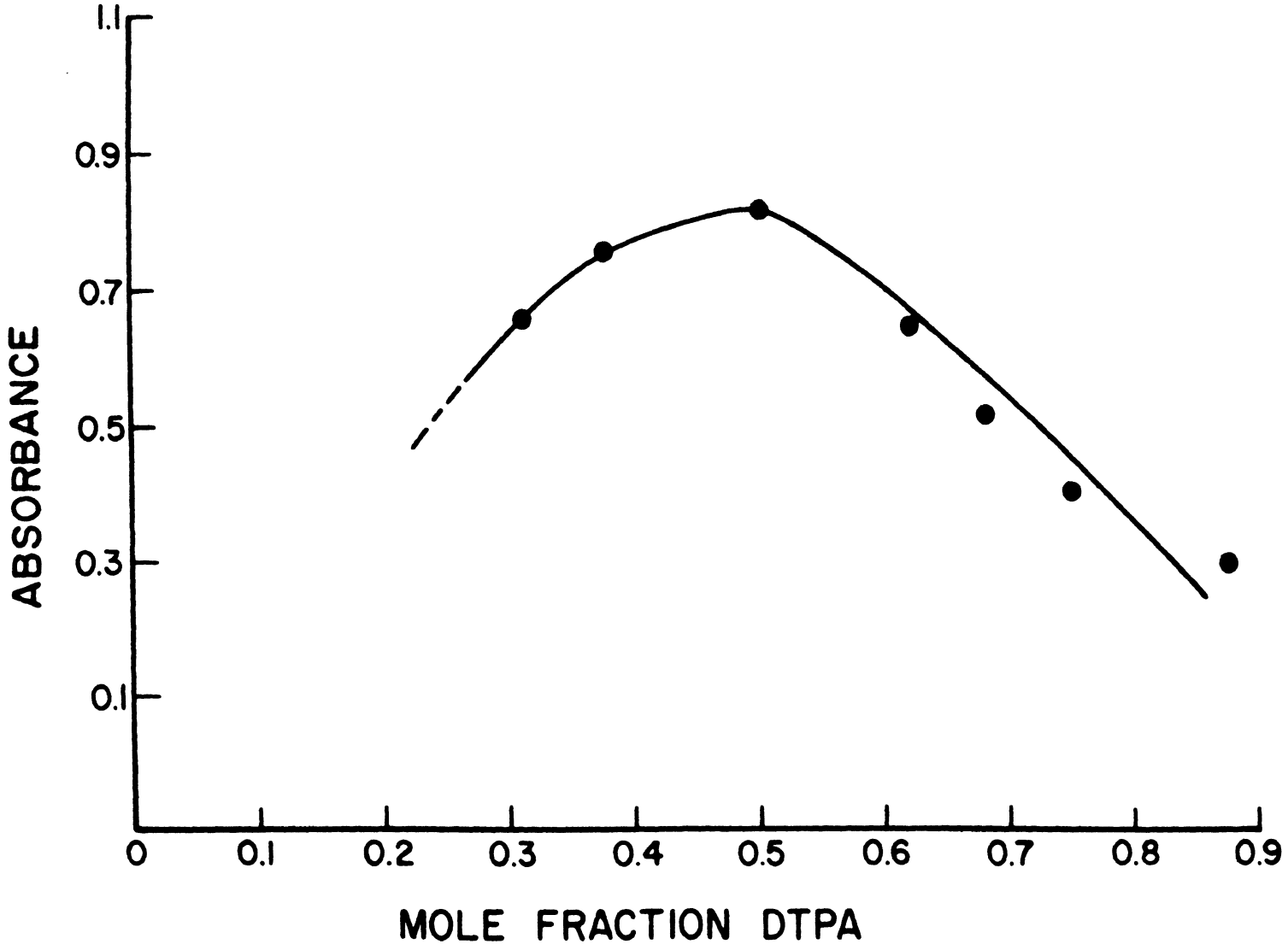

ABSORBANCE
1.1
0.9
0.7
0.5
0.3
0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
MOLE FRACTION DTPA

Fig. 3a

Figure 3b

Molar-Ratio determination of the stoichiometry
of the Ce(IV)-DTPA complex

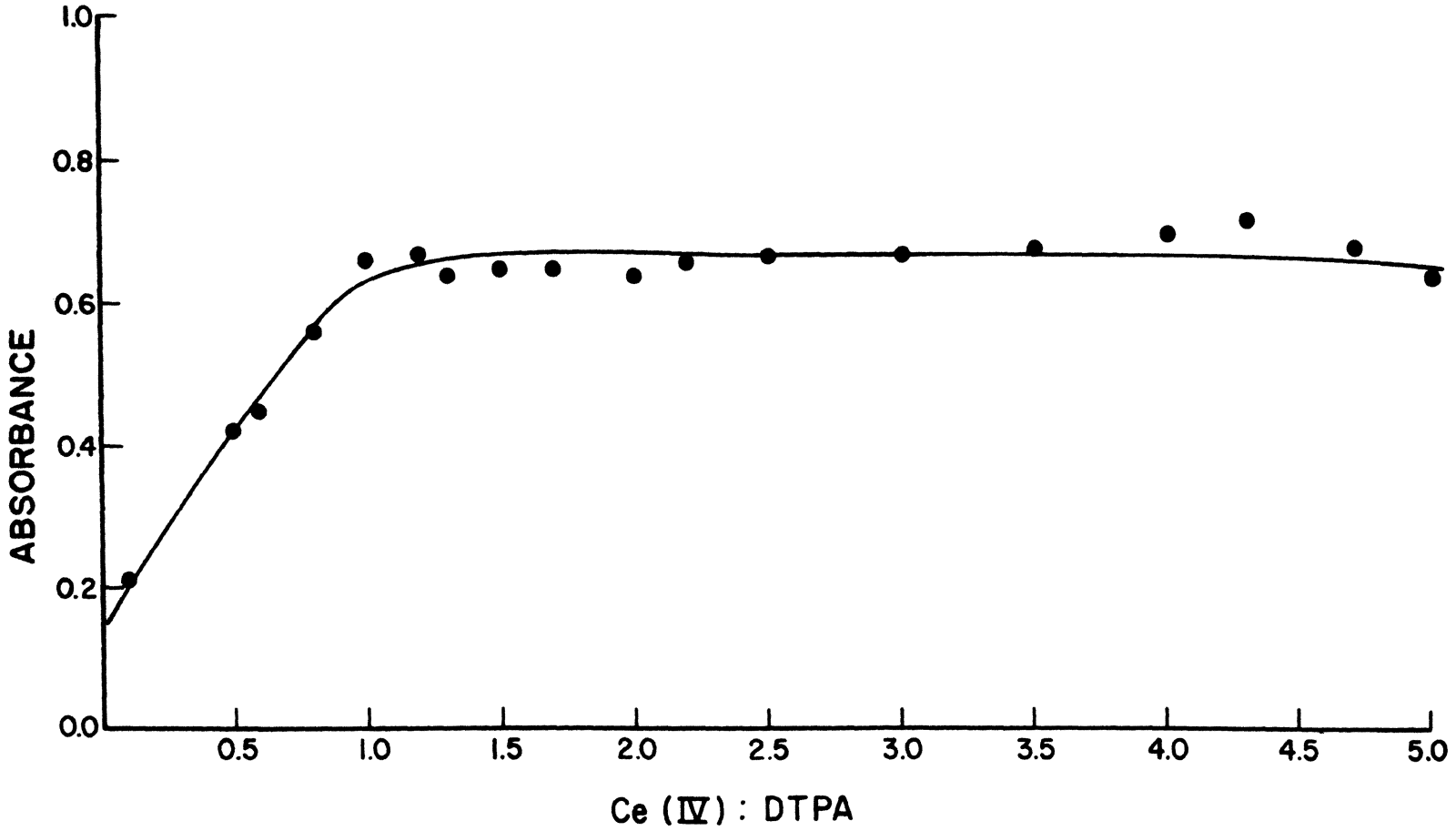

ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Ce (IV) : DTPA

Fig. 3b

measuring the potential of the solution as complexation occurred. It was reasoned that for a redox system where both species form 1:1 complexes whose stability constants are defined by

$$K_{ox} = \frac{[OxY]}{[Ox][Y]}$$

and

$$K_{red} = \frac{[Red\ Y]}{[Red][Y]} ,$$

the potential, E, can be calculated by substitution of the proper expression into the standard Nernst equation:

$$E_c = E^o + \frac{0.059}{n} \log \frac{[OxY]K_{red}}{[RedY]K_{ox}}$$

which reduces to

$$E_c = E^o + \frac{0.059}{n} \log \frac{[Ox]K_{red}}{[Red]K_{ox}}$$

if the stability constants are high enough to consider dissociation of the complex negligible. If [Ox] = [Red], the expression is further simplified. The potential is recorded as the ratio of $M^{n+}/M^{(n-1)+}$ changes during complexation. Because Ce(III) complexes much less strongly than Ce(IV),[14] the standard potential of the complexed couple is much less than that of the uncomplexed one. In this study, the amount of Ce(III) present in the Ce(IV) solutions was extremely small.

As DTPA was added the potential did not change rapidly because Ce(IV) remained in large excess over Ce(III). However a sharp drop in the potential was observed when all the Ce(IV) and finally even Ce(III) was complexed. To be certain that the results were not influenced by the solution of the reactant in excess being titrated, the determinations were made both by titrating Ce(IV) with DTPA, and DTPA with Ce(IV) (Fig. 4). Both graphs show, within 10% reproducibility, that complete complexation occurs at a 1:1 molar ratio. Earlier work with EDTA showed the existence of a 1:1 complex with Ce(IV).[5]

Rates of oxidation of DTPA

Similar to our earlier observation on the Ce(IV)-EDTA reaction,[6] and as Mishra and Gupta,[2a] Dainton and co-workers,[15] and Brubaker and Sincius[16] also observed in their metal ion oxidations with Ce(IV), the influence of the acidity of the media on the rate of the reaction is not linear; rather, an inflection point is observed in the plot of log k_2 *versus* log $[H_2SO_4]$ at about 0.75 M H_2SO_4 (Fig. 5). The position of the maximum is characteristic for both the substrate and the medium. For CDTA, EDTA and NTA oxidations with Ce(IV) in H_2SO_4 media, the maxima occur at 0.05 M, 0.65 M, and 0.40 M respectively.[7] In $HClO_4$, however, the maxima occur at 3.0 M for CDTA, 3.0 M for DTPA, 3.5 M for EDTA and 2.5 M for NTA.[22] The observation is not difficult to explain, qualitatively, in terms of the variations in the concentrations of the active species in the reaction media. In H_2SO_4 media, $Ce(SO_4)^{2+}$ and $Ce(SO_4)_2$ are believed to be the most abundant species;[17] the fraction of Ce(IV) present as the reactive species Ce^{4+} is probably very small. Also, it has been shown that in the high acidity range (1M - 10 M H_2SO_4), there are large concentrations of HSO_4^-,[18] which

Figure 4a

Potentiometric determination of the stoichiometry of the Ce(IV)-DTPA complex; titration with Ce(IV)

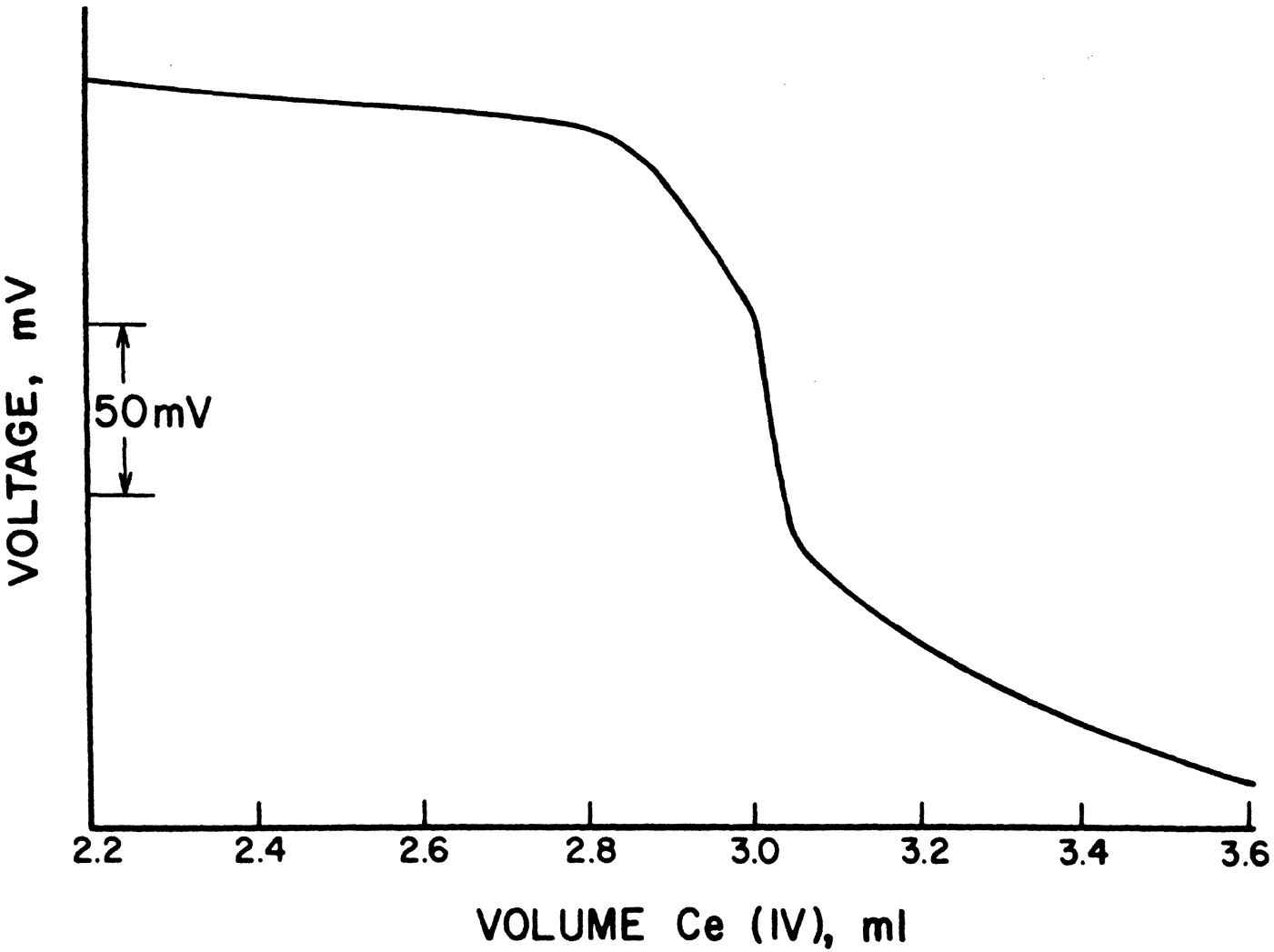


Fig. 4a

Figure 4b

Potentiometric determination of the stoichiometry of the Ce(IV)-DTPA complex; titration with DTPA

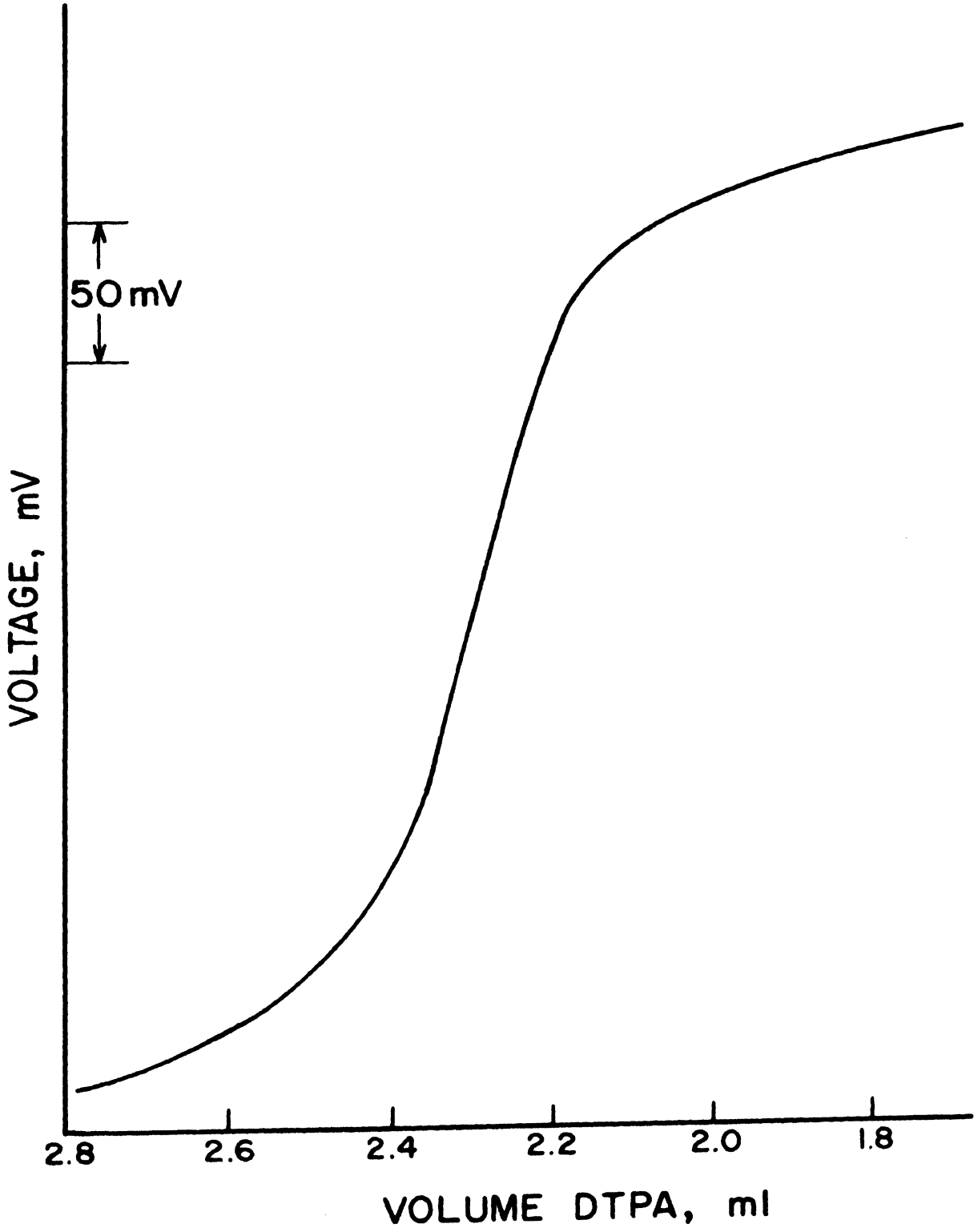


Fig. 4b

Figure 5

Variations in the rate constants for Ce(IV)-DTPA reaction with H_2SO_4 concentration

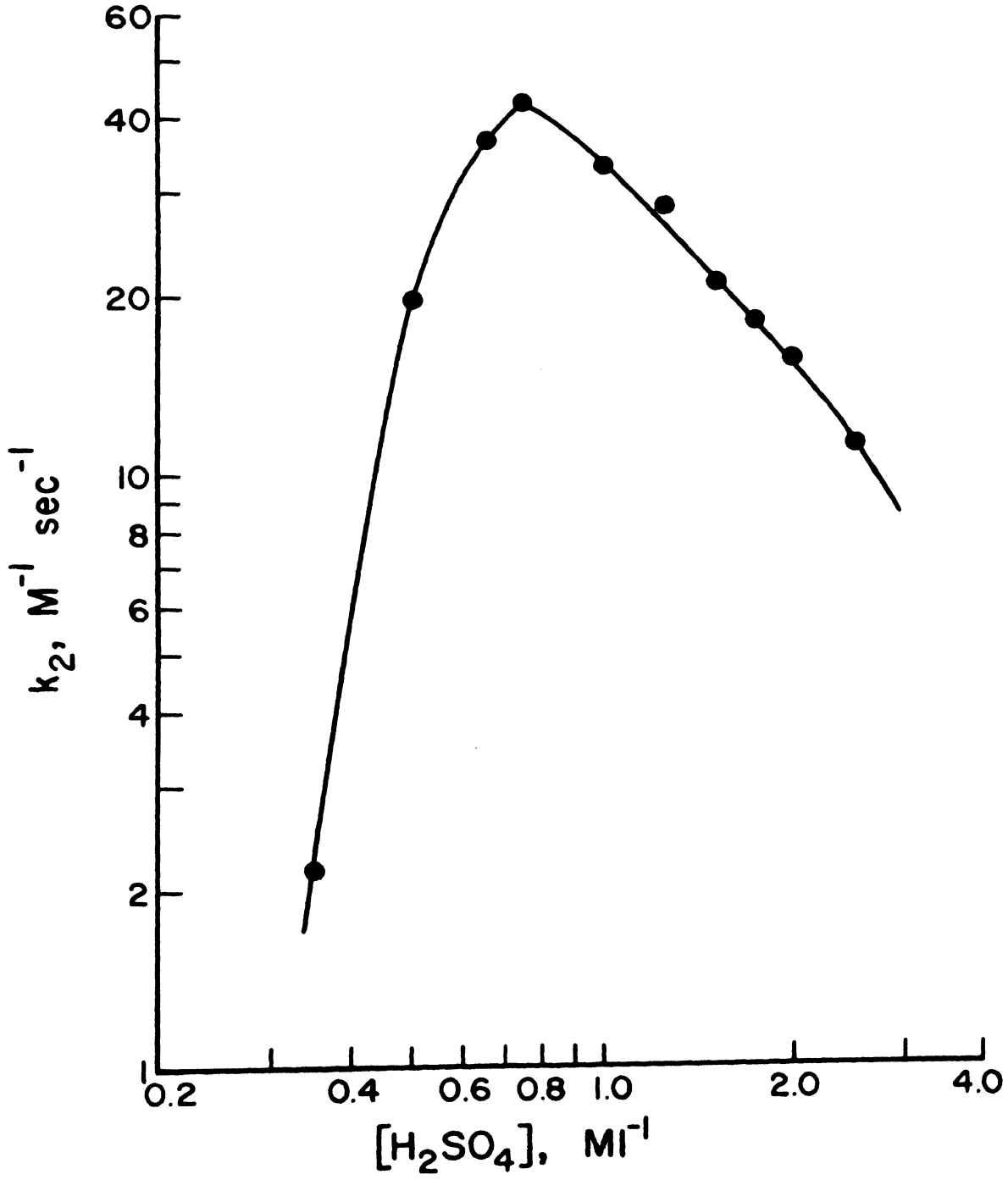


Fig. 5

would complex further with the $Ce(SO_4)_2$ species; thus

$$Ce(SO_4)_2 + HSO_4^- \gtrless Ce(SO_4)_3^{2-} + H^+$$

The increase in the concentration of the heavily complexed $Ce(SO_4)_3^{2-}$ and $HCe(SO_4)_3^-$ species[2b,3,19] as the acidity is increased, would explain the decrease in the rate observed at $[H_2SO_4] > 0.75$ M (Fig. 5). In addition, increased protonation of DTPA, in a manner similar to that reported for EDTA by Olson and Margerum,[20] would also lead to a diminution in the reaction rates since the pairs of electrons on the N-centers would not be available for reduction of Ce(IV).

Because we did not attempt to maintain a constant ionic strength in the media, it is difficult to describe, quantitatively, the ionic species present at any particular acidity. However, at the high acid concentrations used in this work, the concept of ionic strength calculated by conventional formulae becomes vague and inaccurate. It suffices to say that for sulfuric acid, as the stoichiometric concentration is increased, both its protonating power (as measured by the Hammett acidity function H_o), which leads to a preponderance of deactivated DTPA, and its tendency to coordinate heavily with Ce(IV) as shown above, will be simultaneously enhanced. In this work, no attempt was made to determine the extent of each effect separately, but the cumulative decrease in reactivity is reflected clearly in the observed decrease in the rate of reaction beyond 0.75 M H_2SO_4.

In their work in the Ce(IV)-Fe(II) redox system in $HClO_4$, Dainton and co-workers[15] considered the reaction with $Ce(OH)^{3+}$ species, whose concentration is inversely proportional to $[H^+]$, as the one predominating beyond 1 M $HClO_4$. However, it is not clear why the reaction with

Ce^{4+}, which presumably is the most reactive species in the medium, does not dominate the high acidity region. We believe, therefore, that the elegant work of Dainton and co-workers lacks a readily acceptable explanation. Furthermore, attention is drawn to the fact that the claim that the acidity of the medium was maintained at 0.05 M, 0.5 M or 1.0 M $HClO_4$ while the ionic strength was varied up to 3M by addition of $NaClO_4$ (Table 2, reference 15) is not justified. It is a well documented fact that the acidity of the medium changes drastically with the addition of high concentrations of neutral salts.[6,21] A more detailed discussion of this point appears elsewhere.[22]

It is also obvious from the inspection of figure 5, that the order of the reaction varied with respect to the acidity; the slope of the graph of log k_2 vs. log $[H_2SO_4]$ did not remain positive nor was the negative portion equal in magnitude. Table II shows that for $[H_2SO_4] \geq 0.75$ M, a true constant was obtained when the second order rate constant, k_2, was multiplied by $[H_2SO_4]$. These data and the graph in figure 6a show, in this range of acidity, that the rate varied inversely with $[H_2SO_4]$. It was expected at $[H_2SO_4] < 0.75$ M that the observed rate constant for the consumption of Ce(IV), and subsequently k_2, would be affected by the prior formation of the Ce(IV)-DTPA complex. The dependence of the rate on the acidity in that acid range was calculated from the data on the decay of the complex. Table III shows the constant k_2 value obtained when k_2 (observed) for the comples decay was multiplied by $1/[H_2SO_4]^3$. Figure 6b shows the straight line relationship of k_2 vs. $[H_2SO_4]^3$ which indicates that the rate of consumption of Ce(IV) below 0.75 M H_2SO_4 was proportional to $[H_2SO_4]^3$.

TABLE II.-DEPENDENCE OF RATE OF CONSUMPTION OF Ce(IV) ON ACID CONCENTRATION AT $[H_2SO_4] > 0.75\underline{M}$

$[H_2SO_4]$, $\underline{M}$	k_2, M^{-1} sec^{-1}	$k_2 \times [H_2SO_4]$, sec^{-1}
0.75	43.31	32.5
1.00	33.00	33.0
1.25	28.882	36.0
1.50	21.00	31.5
1.75	18.24	31.9
2.00	15.75	31.5
2.50	11.18	28.0

Figure 6a

Graph of observed rate constants versus $1/[H_2SO_4]$ from 0.75M to 2.5M acid

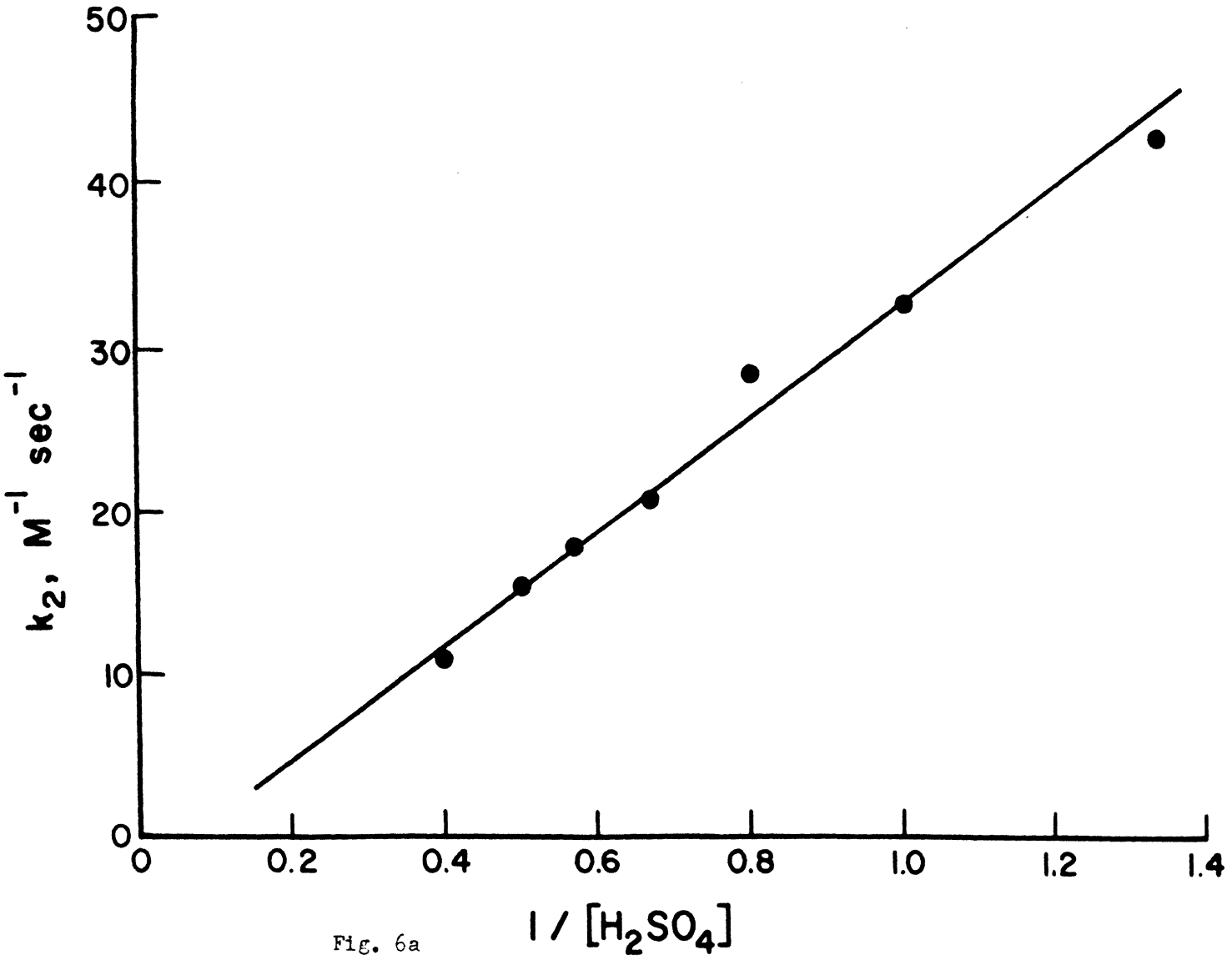


Fig. 6a

TABLE III.-DEPENDENCE OF RATE OF CONSUMPTION OF Ce(IV) ON ACID CONCENTRATION AT $[H_2SO_4] < 0.75\underline{M}$

$[H_2SO_4]$, $\underline{M}$	k_2, M^{-1} sec^{-1}	$k_2 \times [H_2SO_4]^{-3}$, M^{-4} sec^{-1}
0.65	23.10	84.0
0.50	11.13	88.6
0.45	6.93	76.0
0.40	5.12	80.0

Figure 6b

Graph of observed rate constants versus $[H_2SO_4]^3$ from 0.4M to 0.65M acid

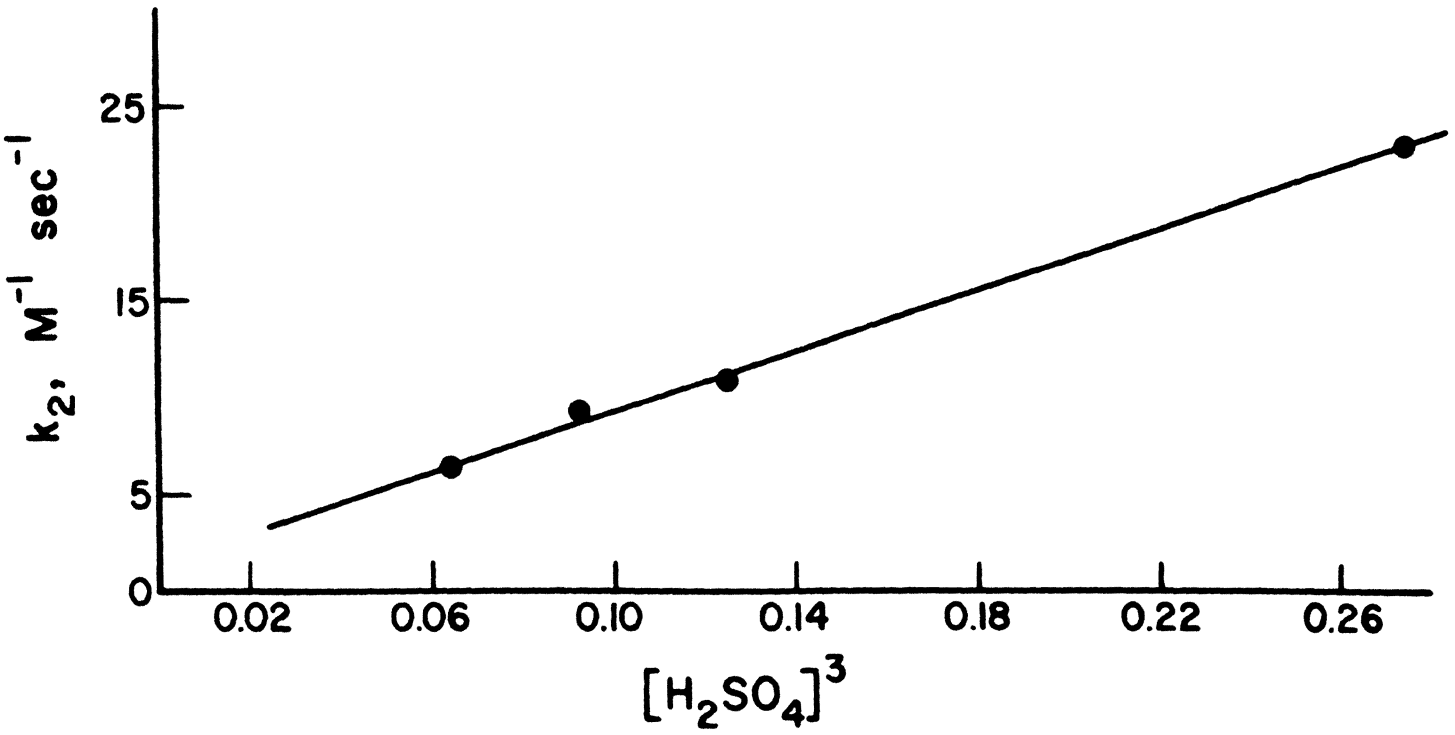


Fig. 6b

Rates of complex formation

In Table IV are listed the rate constants for formation of the Ce(IV)-DTPA complex for varied initial concentrations of reactants. Figure 7 depicts log plots of percent reaction versus time which were linear over 80% of the reaction. These results indicate that the rate of complex formation is proportional to the first power in each reactant; thus,

$$\frac{d[\text{complex}]}{dt} = k[\text{Ce(IV)}][\text{DTPA}]$$

The influence of the acidity of the media on the rate of complex formation is shown in figure 8. The negative slope indicates an inverse relationship of the rate to the acidity. The inverse relationship to the acidity is to be expected because of the following arguments:

1. Protonation of the chelating agent would render it inactive towards complexation with Ce(IV). Complexation of tetravalent metal ions with aminopolycarboxylic acids involves hexadentate chelation.[23] For example, for M(IV)-EDTA complexes may be represented as shown in figure 9.
2. In the transition state for the complexation,

$$M^{4+} + H_4Y \gtrless MY + 4H^+$$

the release of the protons would be hindered if the medium is rich in H^+.

The inverse relationship to the acidity of the media was similar to that observed in the oxidation of HCl by Ce(IV).[2d] It was reported

TABLE IV.-RATES OF FORMATION OF CE(IV)-DTPA COMPLEX IN 0.3M H_2SO_4 AT 264nm, 25°C

[Ce(IV)] x 10^{-4}	[DTPA] x 10^{2}	$t_{\frac{1}{2}}$, m sec	10^{-3} k_2, M^{-1} sec^{-1}
1.0	0.25	220	1.26
1.0	0.50	120	1.15
1.0	0.75	80	1.15
1.0	1.0	60	1.15
0.25	1.0	60	1.15
0.75	1.0	60	1.15
1.0	1.0	60	1.15

Figure 7

Percent reaction versus time for complex formation

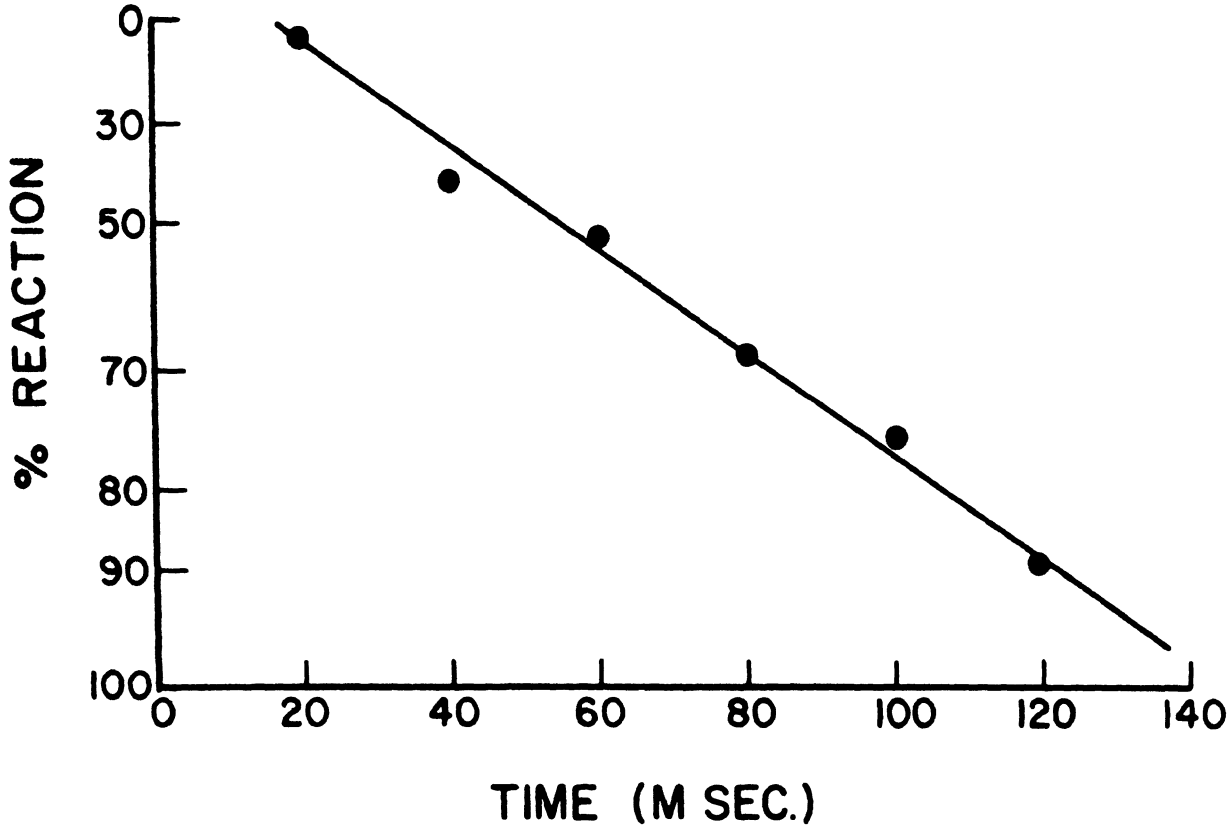


Fig. 7

Figure 8

Dependence of the rate of complex formation on $[H^+]$

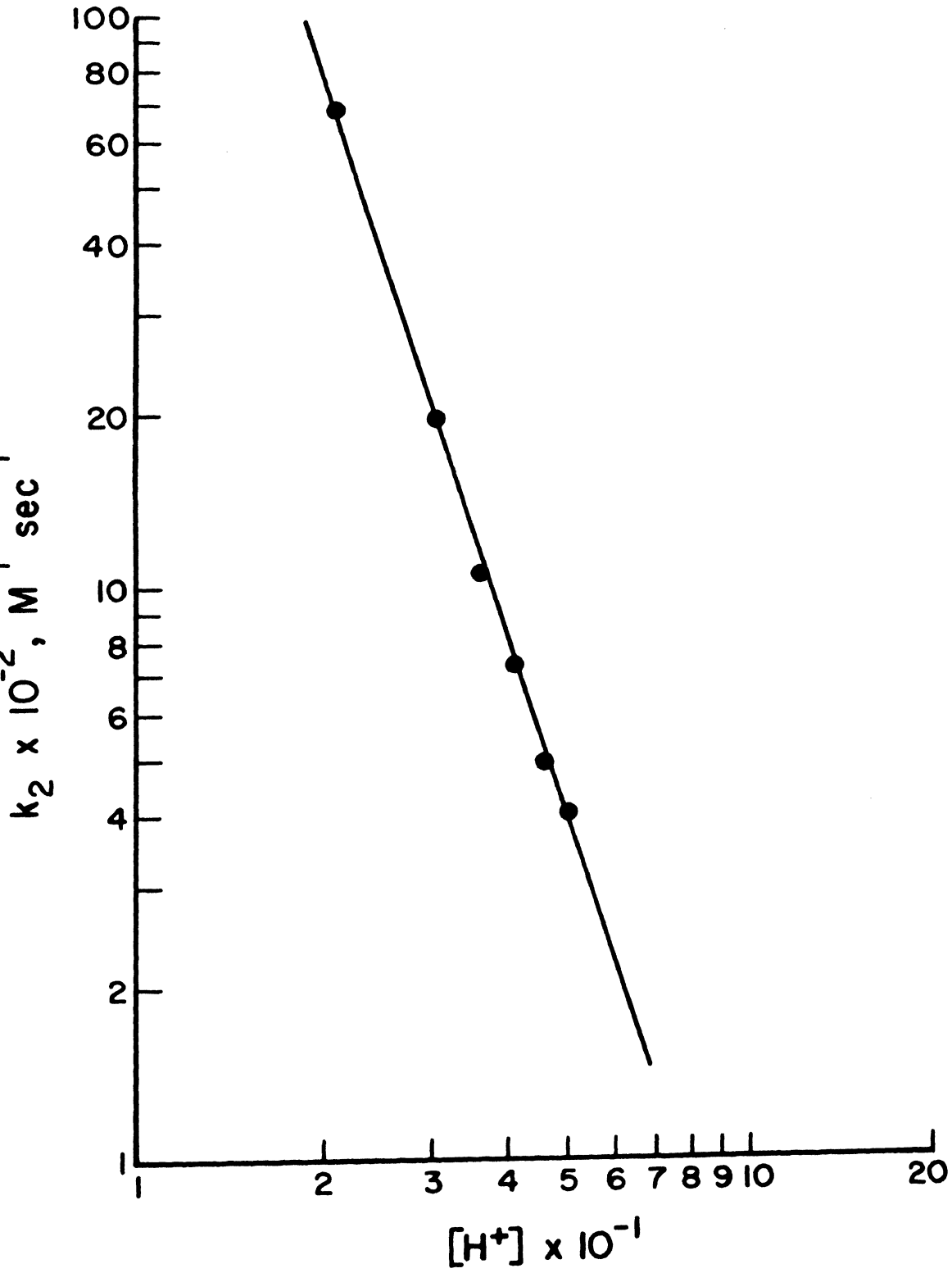

100
80
60
40
20
10
8
6
4
2
1
$k_2 \times 10^{-2}$, M^{-1} sec^{-1}
1
2
3
4
5
6
7
8
9
10
20
$[H^+] \times 10^{-1}$

Fig. 8

Figure 9

Structure of hexadentate M(IV)-EDTA complexes

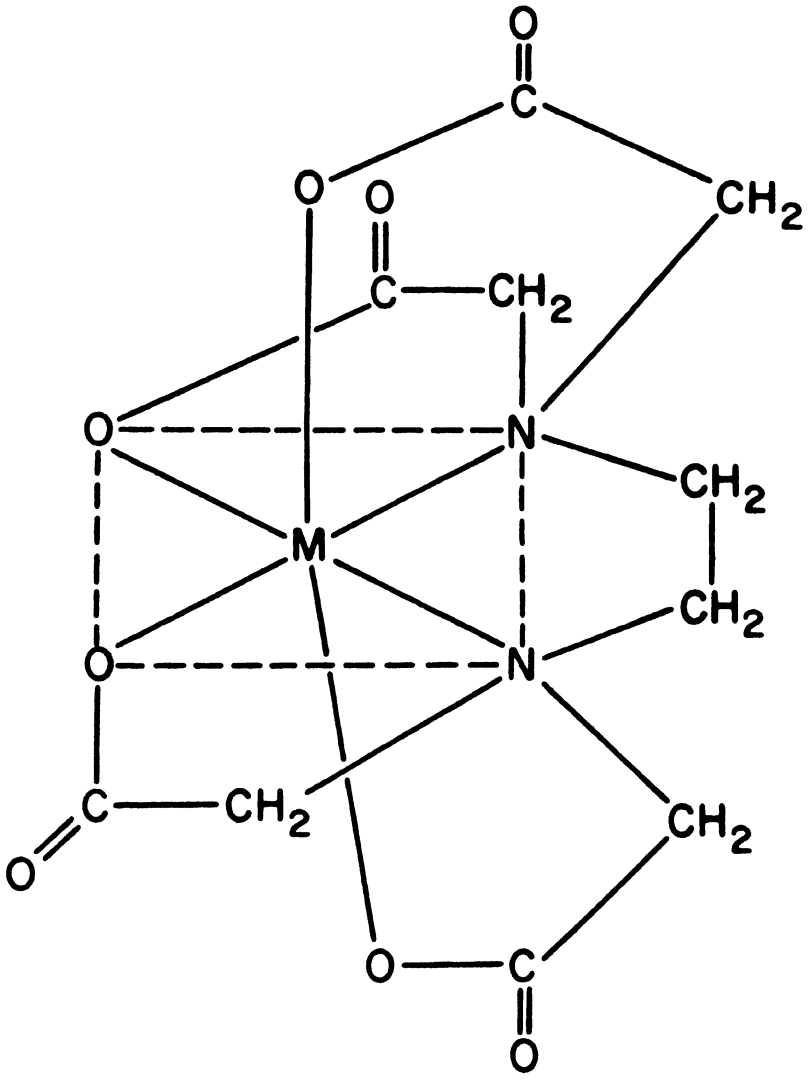


Fig. 9

that the rate of oxidation decreased with increasing HSO_4^- due to the coordination of this species, releasing H^+, with Ce(IV) which interfered with the formation of a Ce(IV)-Cl^- complex required for electron transfer. Mehrotra[2g] has also suggested that increasing $[H_2SO_4]$ decreased the active $Ce(OH)_2^{2+}$ species believed to be necessary for complexation with citric acid. Rao explained his failure to detect a Ce(IV)-EDTA complex in sulfuric acid to be due to the strong Ce(IV)-SO_4 coordination.[3] So far we have observed Ce(IV) complexes with EDTA,[6] DTPA,[8] and NTA[24] in H_2SO_4 media. Although no all-inclusive description has been reported, it is undoubtedly true that for a given process, a weighted combination of these many factors dictate the present and the previous observations depicting the difficulty of complexation with increasing acidity of the media.

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